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Computations of ESR Coupling Constants in Organic Radicals.

II. Nitro Derivatives of the Phenyl Radical

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Berechnungen von ESR Parameter in organischen Radikalen. II. Nitrophenyl-Radikale

Wir beschreiben die nach STO-3G berechneten Molekülstrukturen und ESR-Parameter für zehn Nitrophenyl-Radikale und zwar die drei Mononitrophenyl-Radikale, die sechs Dinitrophenyl-Radikale und das 2,4,6-Trinitrophenyl-Radikal. Es gibt keine experimentellen Daten.

Calcul des constantes de couplage ESR dans des radicaux organiques. II. Dérivés nitrés du radical phényle

On a déterminé par le calcul les constantes de couplage ESR et la structure moléculaire de différents dérivés nitrés du radical phényle. Il s'agit en l'occurrence des trois mononitrophényles, des six dinitrophényles et du 2,4,6-trinitrophényle. Ces calculs ont été effectués d'après STO-3G. Il n'existe pas de résultats expérimentaux.

Summary

We compute the ESR coupling constants and the geometries of a set of nitro derivatives of the phenyl radical. We consider the three mononitrophenyls, the six dinitrophenyls and 2,4,6-trinitrophenyl. The computations are based on the use of the Gaussian 82 Program Package with the STO-3G basis set. There are no experimental data available.

1. Introduction

In the thermal decomposition reactions of energetic materials many of the intermediate products are free radicals. electron spin resonance (ESR) is therefore an effective and popular technique for monitoring those reactions. The detection of free radicals by means of ESR is straightforward but the identification of the free radicals requires the knowledge of their ESR spectra, either from experiments or from theoretical predictions.

In the thermal decomposition of trinitrobenzene and trinitrotoluene many of the intermediate products are nitro derivatives of the phenyl and benzyl radicals. Since no experimental data on the ESR spectra or on the structures of these nitro derivatives are available it would seem to be useful to try and predict them from theoretical methods.

We believe that ESR coupling constants may be derived from unrestricted Hartree-Fock (UHF) computations if the latter are corrected by removing spin contamination. In previous work^(1,2) we presented a simple procedure for removing the quartet spin contamination from a UHF wave function. We applied the procedure to some small organic radicals such as methyl, ethyl, allyl and vinyl⁽¹⁾ and, subsequently, to the phenyl and benzyl radicals and to the benzene and toluene radical anions⁽²⁾.

Since the derivation and the details of our procedure were presented previously^(1,2) we just describe the final results here. We make use of the UHF method and we assume that the differences between the α spin orbitals Φ_i^α and the β spin orbitals Φ_i^β are small when $i = 1, 2, \dots, N$ and that there is one unpaired spin orbital Φ_{N+1}^α . We denote the UHF spin density at the position of nucleus a by $\rho_{\text{UHF}}(a)$ and the corrected spin

density by $\rho_{\text{cor}}(a)$. The relation between ρ_{cor} and ρ_{UHF} is then given by

$$\rho_{\text{cor}}(a) = (1/3)\rho_{\text{UHF}}(a) + (2/3)|\Phi_{N+1}^\alpha(a)|^2 \quad (1)$$

We have computed the ESR coupling constants from Eq. (1) and also the molecular structures of a set of nitro derivatives of the phenyl radical by using the Gaussian 82 Program Package⁽³⁾. The computations were based on the UHF procedure and they all made use of the STO-3G basis sets. The energies and the expectation values $\langle S^2 \rangle$ of the spin operator S^2 are all listed in Table 1.

The derivation of Eq. (1) is based on the assumption that the differences between the α and β spin orbitals are small, which is equivalent with the assumption that the spin contamination of the UHF wave function is also small.

It may be seen from Table 1 that this condition is not satisfied in the present situation since the $\langle S^2 \rangle$ values are all significantly larger than the doublet value 0.75. We feel nevertheless that our work serves a useful purpose even though the accuracy of the results may be open to criticism. First, we consider not just one system but ten different nitrophenyl radicals. We hope that our results will make it possible to detect the similarities and differences between the different radicals. Secondly, our present work represents the best possible *ab initio* computations that can be performed for systems as large as di- and trinitrophenyls. We hope that our theoretical results are

Table 1. Energies (in terms of hartrees) and $\langle S^2 \rangle$ Values of Various Nitrophenyl Derivatives

	E	$\langle S^2 \rangle$
2-nitrophenyl	-428.038 532	2.4903
3-nitrophenyl	-428.039 911	2.4709
4-nitrophenyl	-427.981 082	1.9505
2,3-dinitrophenyl	-628.851 125	3.8029
2,4-dinitrophenyl	-628.835 726	3.4037
2,5-dinitrophenyl	-628.836 463	3.3950
2,6-dinitrophenyl	-628.834 269	3.4009
3,4-dinitrophenyl	-628.848 297	3.8051
3,5-dinitrophenyl	-628.837 819	3.3653
2,4,6-trinitrophenyl	-828.560 951	2.7228

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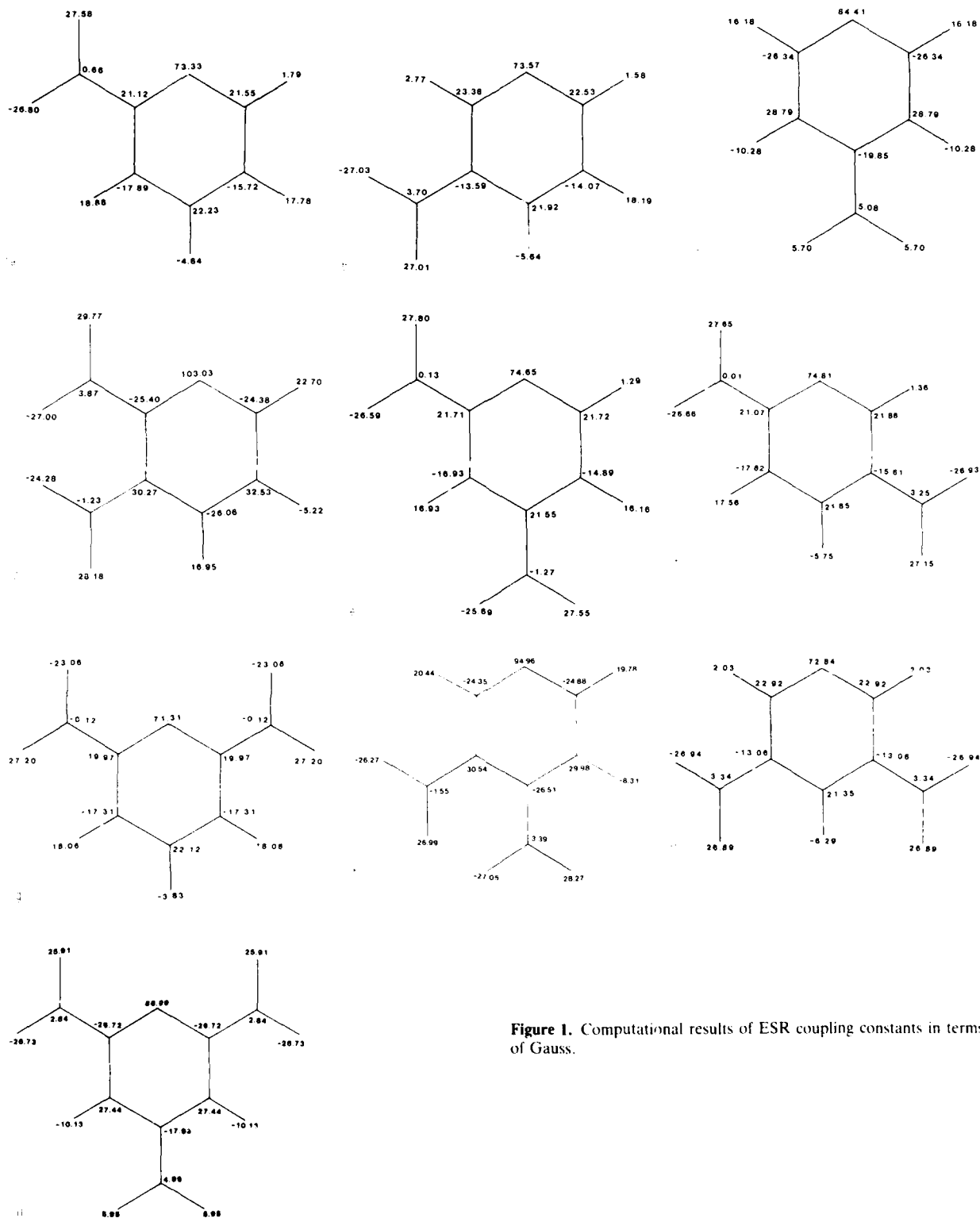


Figure 1. Computational results of ESR coupling constants in terms of Gauss.

helpful in identifying the various ESR spectra since more precise theoretical results are not available at this time.

Recently we also reported theoretical work on the structures of the phenyl and benzyl radicals⁽⁴⁾, based on the use of the

UHF method. We found that our results were more or less consistent with similar work⁽⁵⁾, based on the use of the restricted open-shell Hartree-Fock method (ROHF method). Our best data were derived from the 6-31G basis set for the

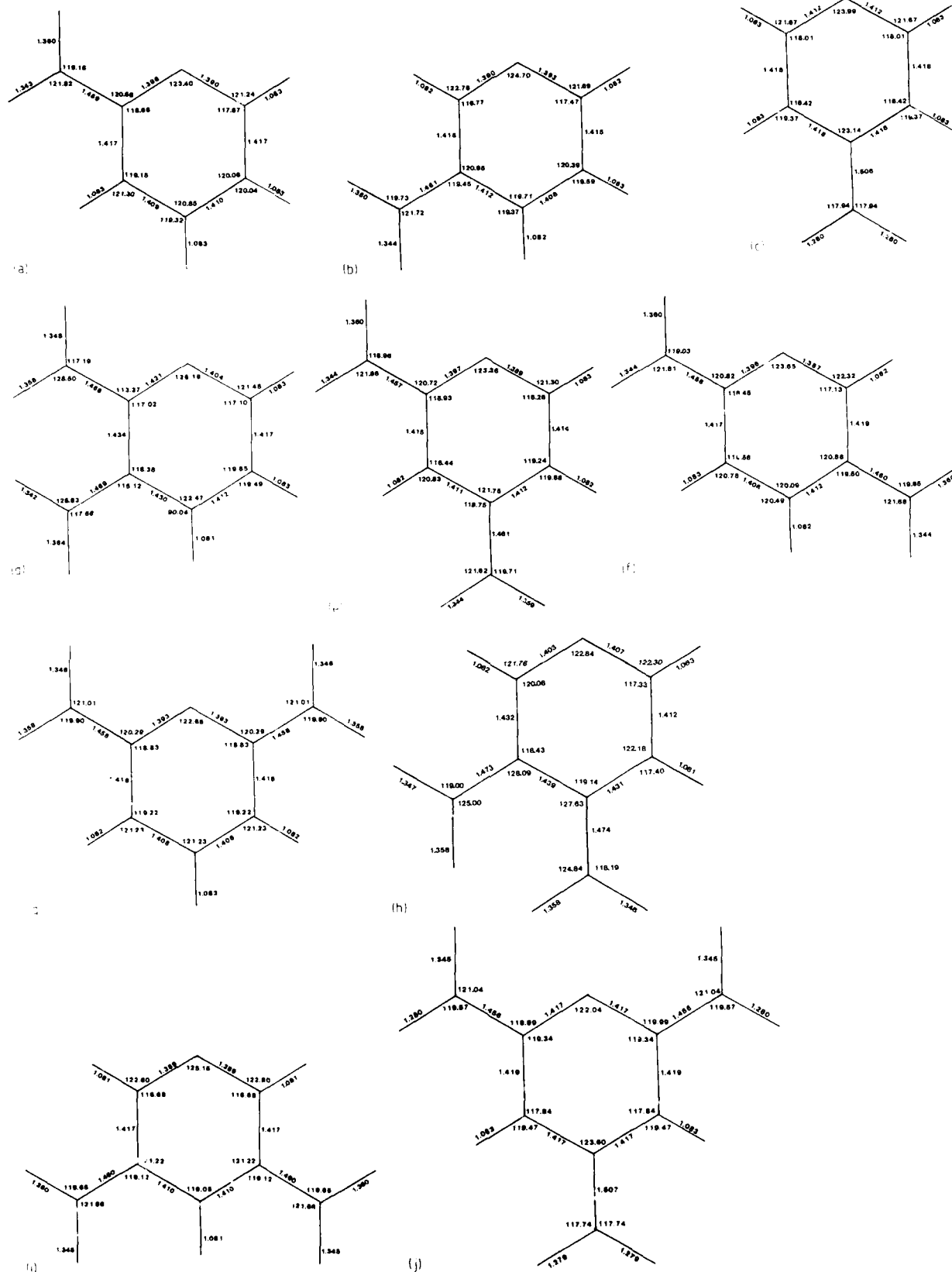


Figure 2. Computed geometries of ten nitrophenyl radicals, bond lengths are expressed in terms of angstrom and bond angles are expressed in terms of degrees.

phenyl radical and from the 4-31G basis set for the benzyl radical. In the case of the phenyl structure the 6-31G results and the STO-3G results were quite similar. The largest discrepancies occurred for the CH bond lengths, the STO-3G values being about 0.01 angström larger than the 6-31G values. However, the two sets of bond angles were almost identical.

It may be instructive also to consider the theoretical energies that are listed in Table 1. In the case of the mononitrophenyls the meta derivative 2-nitrophenyl has the lowest energy and the para derivative 4-nitrophenyl has the highest energy, the difference is 37 kcal/mol. The energy of the meta compound is slightly lower than the energy of the ortho compound, the difference is 0.9 kcal/mol. The energy differences between the various dinitro derivatives are smaller than for the mononitro derivatives, the difference between the lowest energy for 2,3-dinitrophenyl and the highest energy for 2,6-dinitrophenyl is 10.6 kcal/mol. Here the energies become higher the further the nitro groups are separated.

We present our theoretical results for the ESR coupling constants in Figs. 1a to 1j and we discuss them in Sect. 2, the molecular structure results are shown in Figs. 2a to 2j and they are discussed in Sect. 3.

2. ESR Coupling Constants

We computed the ESR coupling constants of the ten nitro derivatives of the phenyl radical by using Eq. (1). The computations are based on the Gaussian 82 Program Package⁽¹⁾ and on the use of the UHF procedure with the STO-3G basis set. It should be noted that the unpaired orbital Φ_{N-1}^{α} is not necessarily the occupied orbital with the highest Hartree-Fock energy. We determined the orbital Φ_{N-1}^{α} from symmetry considerations and from a detailed analysis of all the α and the β spin orbitals.

The ESR coupling constants were derived by evaluating the values of the unpaired orbital Φ_{N-1}^{α} at the positions of the various nuclei by making use of the detailed form of the STO-3G orbitals and of the definitions reported by Hehre, Stewart and Pople⁽⁶⁾. The coupling constants are then expressed in terms of Gauss by using the following conversion factors: 1594.04 for hydrogen, 401.13 for carbon, 230.43 for nitrogen and 1080.88 for oxygen. The results are shown in Figs. 1a to 1j.

We can only speculate about the accuracy of each individual value that we report but we hope to detect certain trends in the values and we hope that these trends are more meaningful than the individual numbers. The phenyl radical is formed by removing one hydrogen atom from the benzene ring and the unpaired electron remains localized around the α carbon that has lost its hydrogen. Consequently the α carbon should have a large ESR coupling constant. This is consistent with our computations, which give values between 73 and 85 for the mononitrophenyls and values between 71 and 103 for the dinitrophenyls. The largest value, 103, occurs for 2,3-dinitrophenyl.

We were surprised to find that the ESR coupling constants of the oxygens in the NO_2 groups were all very similar. With a few exceptions each pair of oxygens in a NO_2 group has values of around +27 and -27 for each pair. The exceptions are found in the para NO_2 groups in the radicals with C_{2v} symmetry, namely in 3-mononitrophenyl and in 2,4,6-trinitrophenyl, here the para oxygen coupling constants are all around +5.8. The nitrogen coupling constants are all small, the largest values of around 5 occur again in the para NO_2 groups of the symmetric radicals.

It should be noted that an ESR experiment does not differentiate between positive or negative values of the ESR coupling constants. Most of the carbon coupling constants seem to fall in the range between 15 and 25 if we consider their absolute values only. Unfortunately, a measurement of the carbon coupling constants does not seem to be of much help in differentiating between the various nitro derivatives. The exceptions are the two dinitrophenyls with adjacent nitro groups, namely 2,3- and 3,4-dinitrophenyl. Here the carbon coupling constants are a bit larger, varying between 24 and 33. However, if we consider the accuracy or lack of accuracy of our theoretical results we must admit that carbon coupling constants do not offer reliable guidelines for identifying the various nitro derivatives.

The coupling constants of the hydrogens are much easier to measure than those of the other atoms. The hydrogen results are therefore the most important. Obviously, an ESR experiment can easily determine the number of hydrogens in a radical and it serves to differentiate between a mono-, a di-, or a trinitrophenyl even if we do not know the values of the coupling constants.

We consider the mono-, di- and tri-derivatives separately. There are only two hydrogens in 2,4,6-trinitrophenyl and their coupling constants are both equal to -10. We did not compute any other trinitro derivatives.

In the case of the mononitro derivatives the ortho and meta radicals have very similar sets of coupling constants, in fact they are so similar that it becomes difficult to differentiate between the two of them. The para derivative has a different set of coupling constants and it is also symmetric so that it should be easy to identify it.

In the case of the dinitro derivatives there are sufficient differences between the six sets of ESR spectra to allow identification. We were unable to detect any obvious trends among the coupling constants other than the fact that pairs of them are equal in the symmetric systems. In three of the radicals (2,3; 2,4; 2,6) there are two large and one small values, in one radical (2,5) there are one large and two small values, in one of them (3,5) they are all small and in one of them (3,4) they are all large. The above features show sufficient differences to permit identification of the various dinitro derivatives.

3. Geometries

In optimizing the geometries of the various nitrophenyl radicals we imposed the condition that the radicals all have a planar structure, other than that we varied all bond lengths and bond angles. The results of the geometry optimizations are presented in Figs. 2a to 2j.

It may be seen that the ten geometries are fairly similar, the exception is those radicals with C_{2v} symmetry and a nitro group in the para position. In these para nitro groups the CN bond length is 1.506 angström and the NO bond lengths are 1.280 angström. In all other nitro groups the CN bond lengths are between 1.46 and 1.47 angström and the two NO bond lengths differ by about 0.015 angström, the larger one being about 1.36 and the smaller one being about 1.345 angström. The CH bond lengths are remarkably constant in all radicals, they vary between 1.081 and 1.083 angström.

The bond angles of the phenyl ring are not strongly affected by the nitro groups. The α carbon usually has the largest bond angle, the average value for the ten radicals is 123.7 degrees. The bond angle at the para position is usually a bit larger than 120 degrees. The largest differences occur for trinitrophenyl

where the α carbon has a bond angle of 122.0 and the para carbon has a bond angle of 123.6 degrees. The ortho and meta bond angles are generally a little smaller than 120 degrees. The presence of a nitro group seems to increase the bond angle by an amount between 0.5 and 1.0 degree as compared to the average value.

4. Final Remarks

We can only speculate about the accuracy of our computational results but we hope that they may be helpful in detecting and identifying the presence of nitrophenyl radicals in organic reactions and that they describe at least the general trends of the ESR spectra and the geometries of those radicals.

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